

## Preparation and Characterization of High-Purity Metal Fluorides for Photonic Applications\*

Wendy M. Patterson,<sup>‡,†</sup> Peter C. Stark,<sup>§</sup> Thomas M. Yoshida,<sup>§</sup> Mansoor Sheik-Bahae,<sup>‡</sup> and Markus P. Hehlen<sup>¶</sup>

<sup>‡</sup>Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico, 87131

<sup>§</sup>Chemistry Division, Los Alamos National Laboratory, Mailstop J964, Los Alamos, New Mexico, 87545

<sup>¶</sup>Materials Science & Technology Division, Los Alamos National Laboratory, Mailstop E549, Los Alamos, New Mexico, 87545

We combine chelate-assisted solvent extraction (CASE) and hot hydrogen fluoride gas treatment to enable a general method for the preparation of high-purity binary metal fluorides. The fluorozirconate glass ZBLAN:Yb<sup>3+</sup> (ZrF<sub>4</sub>–BaF<sub>2</sub>–LaF<sub>3</sub>–AlF<sub>3</sub>–NaF–InF<sub>3</sub>–YbF<sub>3</sub>), a solid-state laser-cooling material, is used as a test case to quantitatively assess the effectiveness of the purification method. The reduction of transition-metal and oxygen-based impurities is quantified directly by inductively coupled plasma mass spectrometry (ICP-MS) and indirectly by laser-induced cooling, respectively. The concentrations of Cu, Fe, Co, Ni, V, Cr, Mn, and Zn impurities in the ZrCl<sub>2</sub>O precursor solution were measured individually by ICP-MS at various stages of the purification process. CASE was found to reduce the total transition-metal concentration from 72500 to ~100 ppb. Laser cooling was most efficient in ZBLAN:Yb<sup>3+</sup> glass fabricated from CASE-purified metal fluoride precursors, confirming the results of the ICP-MS analysis and demonstrating the effectiveness of the purification methods in a finished optical material. High-purity metal fluorides prepared by the methods presented herein will enable new high-performance optical materials for solid-state optical refrigerators, crystals for vacuum ultraviolet (VUV) spectroscopy of the Thorium-229 nucleus, VUV optics, fibers, and thin-film coatings.

### I. Introduction

FLUORIDE crystals and glasses are of interest to a wide range of photonic applications including bulk optics for vacuum ultraviolet (VUV) photolithography,<sup>1</sup> optical fibers for high power or long-haul transmission,<sup>2,3</sup> host materials for lasers, and optical amplifiers,<sup>2,4–7</sup> scintillators,<sup>8,9</sup> up-conversion phosphors,<sup>10</sup> solid-state optical refrigerators,<sup>11</sup> and emerging crystals for optical spectroscopy of the Thorium-229 nucleus.<sup>12</sup> These applications take advantage of the high bandgap energy (>6 eV) and/or the low optical phonon energies (<500 cm<sup>–1</sup>) of fluorides. The attractive intrinsic properties of fluorides, however, can be substantially degraded by the presence of impurities. Transition-metal ions have optical transitions in the ultraviolet (UV) and visible spectral regions<sup>13,14</sup> that lead to undesired background absorption as well as non-radiative quenching of excited states via energy

transfer, even at trace concentrations.<sup>15</sup> Likewise, oxygen-based impurities such as metal oxides, oxyfluorides, hydroxyl ions (OH<sup>–</sup>), and water can degrade material performance by introducing UV absorptions<sup>16,17</sup> and high-energy vibrational modes that enhance multi-phonon relaxation rates of excited states.<sup>18–23</sup> The slow growth of fluoride crystals can reduce the concentration of some of these impurities in the final material. Fluoride glasses on the other hand are more susceptible to incorporation of impurities because a glass generally contains all of the species that were present in the melt from which it was quenched.

Solid-state laser coolers are a class of photonic materials with particularly demanding purity requirements. Laser cooling removes thermal energy from a solid by anti-Stokes fluorescence and thereby reduces its temperature. A comprehensive introduction to solid-state laser refrigeration has been given elsewhere.<sup>11</sup> Impurities can introduce several undesirable processes that cause internal heating and therefore degrade the laser-cooling performance. The primary quenching mechanism is by non-radiative energy transfer from the excited laser-cooling ion (e.g. Yb<sup>3+</sup>) to transition-metal impurities (such as Cu<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>) which subsequently decay non-radiatively and thereby produce undesired internal heating of the solid.<sup>11,15</sup> Furthermore, impurities with high-energy vibrational modes (such as OH<sup>–</sup> and H<sub>2</sub>O) can quench the excited state of the laser-cooling ion via multi-phonon relaxation. Finally, some impurities can also directly absorb at the pump wavelength causing heating in the form of background absorption. Reducing transition-metal and oxygen-based impurities suppresses these undesired impurity-induced decay channels and thus improves the laser-cooling performance. Estimates for Yb<sup>3+</sup>-doped fluorozirconate glass ZBLAN (ZrF<sub>4</sub>–BaF<sub>2</sub>–LaF<sub>3</sub>–AlF<sub>3</sub>–NaF) indicate that transition-metal and OH<sup>–</sup> impurities in excess of ~100 parts-per-billion (ppb) begin to compromise laser-cooling performance.<sup>15</sup> Other applications have similarly stringent purity requirements.<sup>12</sup> The preparation of high-purity binary fluoride starting materials is therefore critical toward enabling the desired performance of many fluoride optical materials.

There currently exists no single comprehensive method for the purification and synthesis of ultra-pure metal fluorides. The chemical inertness and relatively high melting temperatures of fluorides prevent the use of many of the standard purification methods. Some successes have been achieved by sublimation and distillation of ZrF<sub>4</sub> as well as zone refining,<sup>24,25</sup> but these methods are not applicable to many of the other metal fluorides of interest. Reactive gas atmospheres of CF<sub>4</sub>, NF<sub>3</sub>, SF<sub>6</sub>, Cl<sub>2</sub>, or CCl<sub>4</sub> have been used during fluoride melting to reduce oxygen-based impurities,<sup>26,27</sup> but these molecules themselves often incorporate the final glass and

J. Ballato—contributing editor

Manuscript No. 29422. Received March 08, 2011; approved April 21, 2011.

\*Based in part on the thesis submitted by W. M. Patterson for the PhD degree in Optical Science and Engineering, University of New Mexico, Albuquerque, NM 87131, (2009)

<sup>†</sup>Author to whom correspondence should be addressed. e-mail: wendy5@unm.edu

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>2011</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2011 to 00-00-2011</b>	
4. TITLE AND SUBTITLE <b>Preparation and Characterization of High-Purity Metal Fluorides for Photonic Applications</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>University of New Mexcio,Department of Physics and Astronomy,Albuquerque,NM,87131</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>6</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

can be detrimental in many applications. Vapor-phase processes appear attractive due to the success of chemical vapor deposition (CVD) in purifying silica for fiber technology. Although some studies have obtained encouraging results,<sup>28–30</sup> the preparation of bulk quantities of fluoride glasses by CVD is difficult because of the high evaporation temperature of many binary fluorides. Therefore, a comprehensive purification strategy must target the chemistry *before* the formation of the metal fluoride. One such method is chelate-assisted solvent extraction (CASE). In this process, an organic chelate is introduced to bind to undesired metal ions in an aqueous phase and to transfer the resulting metal-chelate complexes into a second organic phase. CASE is widely used in analytical chemistry to pre-concentrate heavy metals for trace analysis.<sup>31–36</sup> Alternatively, CASE can remove metal-ion impurities from an aqueous solution of a desired metal ion and thus achieve purification. Ling *et al.* have used the latter approach with ammonium-pyrrolidinedithio-carbamate (APDC) as the chelate and methyl-isobutylketone (MIBK) as the organic phase to reduce Co, Ni, and Cu to <5 ppb, and Fe to <10 ppb in zirconium solutions.<sup>36</sup>

The goal of the present study is to develop APDC/MIBK as a single chelate/organic solvent system suitable for the individual purification of all components of the laser-cooling glass ZBLANI:Yb<sup>3+</sup> (ZrF<sub>4</sub>–BaF<sub>2</sub>–LaF<sub>3</sub>–AlF<sub>3</sub>–NaF–InF<sub>3</sub>–YbF<sub>3</sub>). The ability to perform purification of all respective metal fluoride precursors with a single chelate/solvent system minimizes the development effort and greatly simplifies processing. Specifically, we (1) expand CASE to the purification of main group elements (Zr, Ba, Al, Na, In) and the rare earths (La, Yb), (2) advance the method to include the precipitation, drying, and fluorination of the resulting binary metal fluorides, and (3) quantitatively verify the impact of reduced impurities on the performance of a ZBLANI:Yb<sup>3+</sup> optical refrigerator material synthesized from the purified binary metal fluorides.

## II. Experimental Procedure

### (1) General Procedures

Concentrated hydrofluoric acid and hot hydrogen fluoride gas are toxic and can pose a severe health hazard if handled improperly. Hydrofluoric acid (HF, 49%), nitric acid

(HNO<sub>3</sub>, 69%), and hydrochloric acid (HCl, 33%) were doubly distilled and trace-metal grade (GFS Chemicals, Powell, OH). Ultra-high purity (UHP) water (Inorganic Ventures, Christiansburg, VA) and electronic grade 4-Methyl-2-pentanone (MIBK; Acros Organics, Geel, Belgium) were used. All processing occurred in a fume hood inside a Class 100 clean room. Acid evaporations were performed in a distillation still constructed from perfluoroalkoxy (PFA) resin, with the evaporation side being heated to 190°C by a temperature-controlled heating jacket. All vessels and utensils were cleaned by leaching them in dilute nitric acid at elevated temperatures for several days before use. A 1% solution of APDC chelate (Acros Organics) in UHP water was prepared daily by dissolving 1 g of APDC in 100 mL of water and filtering through a < 0.2 µm pore size nylon syringe filter. A buffer solution was prepared by dissolving 50 g of ammonium acetate (Fluka, Sigma-Aldrich, St. Louis, MO; 99.995%) in 100 mL of UHP water and adding acetic acid to adjust the pH to ~4.5.

### (2) Chelate-Assisted Solvent Extraction (CASE) and Precipitation of Metal Fluoride

Processing details are summarized in Table I. The general strategy involved dissolving the starting material in acid or UHP water, buffering, and filtering through a < 0.2 µm pore size Nylon syringe filter into a separatory funnel to carry out CASE at room temperature. A quantity of 5 mL of 1% APDC solution was added and the mixture was briefly shaken. A quantity of 35 mL of MIBK was added, and the two-phase system was shaken vigorously for 1 min, and the aqueous phase was collected after the system had equilibrated for 10 min. This extraction procedure was repeated three times, the final aqueous phase was collected in a polytetrafluoroethylene (PTFE) beaker, and HF acid was added to precipitate the metal fluoride. To remove residual buffer, excess acid, and non-fluoride water-soluble compounds, 30 mL of UHP water was added to the metal fluoride precipitate, the slurry was sonicated for 1 h, and the water was decanted. This washing procedure was repeated three times, and the metal fluoride was dried in a PTFE beaker at 190°C. In the case of Zr, the initial ZrCl<sub>2</sub>O·8H<sub>2</sub>O solution was boiled and water was added continuously (350 mL) to raise

**Table I. Precursors for the Melt Synthesis of ZBLANI:Yb<sup>3+</sup> Glass. The First Column Shows the Vendor-Quoted Cationic Purity of Commercially Available Metal Fluorides. The Subsequent Columns Show the Details of the Chelate-Assisted Solvent Extraction (CASE) and Metal Fluoride Precipitation Steps Described in Sections II(1) and II(2). Note that for Ba and La, In, Yb the Respective Chloride and Nitrate is First Formed Before Dissolving in UHP Water for Subsequent CASE**

Fluoride, purity (%)	CASE starting material, vendor, purity (%)	Dissolution of starting material	pH for CASE	Quantity (g)		
				Starting material	Buffer	HF
ZrF <sub>4</sub> , 99.5%	ZrCl <sub>2</sub> O·8H <sub>2</sub> O, Alfa Aesar, 99.9985%	68 g UHP water	2.5	41	60	28.0
BaF <sub>2</sub> , 99.99%	BaCO <sub>3</sub> , Strem Chemicals, 99.999%	(1) 30 g HCl (slow) (2) 34.5 g UHP water	3.8	10	33	42.5
LaF <sub>3</sub> , 99.9%	La <sub>2</sub> O <sub>3</sub> , Metall Rare Earth Ltd, 99.99993%	(1) 38 g HNO <sub>3</sub> (2) 27 g UHP water	3.3	2.9	18.5	21.4
AlF <sub>3</sub> , 99.9%	AlCl <sub>3</sub> ·6H <sub>2</sub> O, Alfa Aesar, 99.99956%	27 g UHP water	2.8	6.0	50	40.6
NaF, 99.5%	Na <sub>2</sub> CO <sub>3</sub> , Sigma-Aldrich, 99.997%	32 g UHP water	5.0	7.0	73	40.5
InF <sub>3</sub> , 99%	Indium metal, Alfa Aesar, 99.9999%	(1) 100 g of HNO <sub>3</sub> , (slow) (2) 32 g UHP water	2.5	7.7	25	25.4
YbF <sub>3</sub> , 99.9%	Yb <sub>2</sub> O <sub>3</sub> , Metall Rare Earth Ltd, 99.99992%	(1) 35.5 g HNO <sub>3</sub> (2) 22 g UHP water	3.6	2.5	21.3	21.3

Alfa Aesar, Ward Hill, MA.

Strem Chemicals, Newburyport, MA.

Metall Rare Earth Ltd, New Territories, Hongkong, China.

Sigma-Aldrich, St. Louis, MO.

the pH to  $\sim 1$  to reduce the amount of buffer needed. Both Zr and In precipitated as the respective ammonium fluoride compounds, which were thermally decomposed in glassy-carbon beakers to  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  (at  $370^\circ\text{C}$ ) and  $\text{InF}_3$  (at  $460^\circ\text{C}$ ), respectively. Ba was first converted to the chloride and then dissolved in water. La, Yb, and In were first converted to the respective nitrate and then dissolved in water. In the case of La, slow, drop-wise addition of HF acid under stirring (550 rpm, PTFE stir bar) favored the precipitation of  $\text{LaF}_3$  over the competing precipitation of ammonium compounds.

### (3) Drying of Metal Fluorides in Hydrogen Fluoride (HF) Gas

Precipitated metal fluorides were dried and fluorinated in HF gas at  $300^\circ\text{C}$  using a custom apparatus adapted from Burkhalter *et al.*<sup>37</sup> and Krämer *et al.*<sup>38</sup> The fluorides were contained in glassy-carbon boats, inserted into a glassy-carbon-lined Inconel Alloy 600 steel reaction tube, and placed in a horizontal tube furnace. HF gas was generated by  $\text{KHF}_2$  decomposition in a separate vertical tube furnace. 25.6 g of HF gas was produced in 19 h by decomposing 100 g of previously dried  $\text{KHF}_2$  (dried at  $190^\circ\text{C}$  for  $>60$  h in vacuum) via heating to  $390^\circ\text{C}$  at 135 K/h, to  $440^\circ\text{C}$  at 4.5 K/h, and to  $480^\circ\text{C}$  at 8.3 K/h. A mass-flow controller (Aalborg, Orangeburg, NY) maintained a constant flow rate of semiconductor grade argon (Ar) to provide an estimated 7 vol% average HF concentration. Ar/HF exhaust gas was bubbled through a calcium hydroxide solution to remove HF by precipitation of  $\text{CaF}_2$ .

### (4) Glass Formation and Sample Preparation

Table II summarizes the nominal compositions of the ZBLANI:Yb<sup>3+</sup> glasses prepared in this study. The dried metal fluorides were combined, and glass melting occurred in a covered glassy-carbon crucible inside an argon dry box which was controlled to  $<0.1$  ppm of  $\text{O}_2$  and  $<0.6$  ppm  $\text{H}_2\text{O}$  and was equipped with HEPA filters. A practical limit for the ZBLANI:Yb<sup>3+</sup> melting temperature is set by the volatilization rate of  $\text{ZrF}_4$ , which sublimates at  $600^\circ\text{C}$ . To minimize sublimation of  $\text{ZrF}_4$  from the batch of precursor fluoride powders before melting occurred, the batch was inserted into a preheated ( $750^\circ\text{C}$ ) furnace to effect rapid melting. The batch was melted for 5 h and cooled to  $550^\circ\text{C}$  at 10 K/min before the melt was cast into a platinum mold at room temperature. The glass was annealed by heating to just below the glass transition temperature of  $250^\circ\text{C}$  at 2 K/min, holding for 1 h, and cooling to room temperature at 0.2 K/min. Sample 1 was fabricated from commercial metal fluoride precursors that first required drying and fluorination in hot HF gas to reduce oxide impurities that otherwise caused significant crystallization. The annealed glass was cut into a rectangular parallelepiped with an ethylene glycol-cooled dia-

mond saw, and all sides were polished. The two parallel sides designated to receive the pump laser beam were further polished by a wet process.  $\text{Al}_2\text{O}_3$  particles (sizes from 12 to  $0.05\ \mu\text{m}$ ) were suspended in emulsions of water-free ethylene glycol and glycerin, adjusting the viscosity by the amount of glycol. Polishing slurries were prepared daily, and the wax mounted samples were polished with slurries of decreasing particle size on fine-textured, non-abrasive polishing cloths. Samples were sonicated in optical grade methanol for several hours and cleaned with lens paper before use.

### (5) Sample Characterization

A high-resolution magnetic sector inductively coupled plasma mass spectrometer (ICP-MS, Thermo Electron Corporation Element II) was used to measure trace metals at various stages during the CASE process. The ICP-MS had low parts-per-trillion (ppt) sensitivity with linearity over nine orders of magnitude. Samples were collected from the  $\text{Zr}^{4+}$  solution immediately before CASE, after each of the CASE steps, and from the UPH water. All samples except the UPH water were digested to reduce interference of the ammonium acetate buffer with the ICP-MS. Digestion involved boiling of the sample in 1:2 HCl: $\text{HNO}_3$  until near evaporation, cooling, addition of hydrogen peroxide, and evaporation to  $\sim 1$  mL. This was repeated twice and followed by 20-fold dilution with UHP water. The instrument was calibrated using certified  $^{63}\text{Cu}$ ,  $^{56}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{58}\text{Ni}$ ,  $^{60}\text{Ni}$ ,  $^{51}\text{V}$ ,  $^{52}\text{Cr}$ ,  $^{55}\text{Mn}$ , and  $^{64}\text{Zn}$  standards. The total concentration of each metal was obtained by scaling the measured isotope by its terrestrial abundance. A quantity of 1 ppb of  $^{115}\text{In}$  was added to each sample as an internal standard to eliminate sample matrix effects and to account for variations in background readings. The phase purity of each metal fluoride was verified by a commercial X-ray diffractometer (XRD, Rigaku, The Woodlands, TX). Two-band differential luminescence thermometry (TBDLT)<sup>39,40</sup> was used to measure local laser-induced cooling or heating in ZBLANI:Yb<sup>3+</sup> samples.

## III. Results and Discussion

### (1) Binary Metal Fluoride Synthesis Strategy

Table I summarizes the starting materials used for the preparation of ZBLANI:Yb<sup>3+</sup> glass by a melting process. The commercial binary fluorides  $\text{ZrF}_4$ ,  $\text{BaF}_2$ ,  $\text{LaF}_3$ ,  $\text{AlF}_3$ ,  $\text{NaF}$ ,  $\text{InF}_3$ , and  $\text{YbF}_3$  have substantial transition-metal and oxygen-based contaminations. A ZBLANI:Yb<sup>3+</sup> glass produced from these precursors would contain several thousands of ppm of transition-metal contamination, which is unacceptable in comparison to the target of  $\sim 100$  ppb. As shown in Table I, metal oxide, carbonate, chloride, and elemental precursors on the other hand are commercially available in significantly higher purity and can serve as precursors for the synthesis of binary metal fluorides. But without further puri-

**Table II.** Summary of the Yb<sup>3+</sup>-Doped ZBLANI Samples Synthesized and Characterized in this Study. The Typical Batch Size was 4 g

Sample No.	Yb <sup>3+</sup> (mol%)	ZBLANI composition (mol%)	Description and preparation notes
1	1	54–21–3.5–3.5–16.5–0.5	Produced from commercial metal fluoride precursors without further purification. Some bulk scattering.
2	1	54–21–3.5–3.5–16–1	First generation CASE process. Some bulk scattering.
3	1	53–20–3–3–17.5–2.5	Second generation CASE process. Improved melting/casting scheme. Excellent optical quality.
4	1	53–20–3–3–17.5–2.5	Third generation CASE process. Lower HF gas drying temperature. Excellent optical quality.
5	2	53–20–2–3–17.5–2.5	Same as sample 4 but with 2% Yb <sup>3+</sup> doping.
6	1	53–20–3–3–17.5–2.5	Same as sample 4 but $\text{ZrF}_4$ purified by sublimation rather than solvent extraction.
7	2	Unknown	Commercial ZBLAN:Yb <sup>3+</sup> sample from IPG Photonics.

**Table III. Transition-Metal Concentration (ppb) in a  $\text{ZrCl}_2\text{O}$  Solution Before, During, and After Purification by CASE. These Data are also Illustrated in Fig. 1.**

	Cu	Fe	Co	Ni	V	Cr	Mn	Zn	Total
Before CASE	0	51600	177	7130	32.8	2140	3820	7640	72540
After 1st CASE step	0	711	3.09	143	5.07	93.9	26.4	454	1436
After 2nd CASE step	0	83.0	0.078	0	0.695	17.5	15.1	0	116
After 3rd CASE step	0	58.5	0	0	1.10	18.6	2.56	33.9	115
Ultra-high purity (UHP) $\text{H}_2\text{O}$	0	0	0	0	0	0.147	0	0	0.147

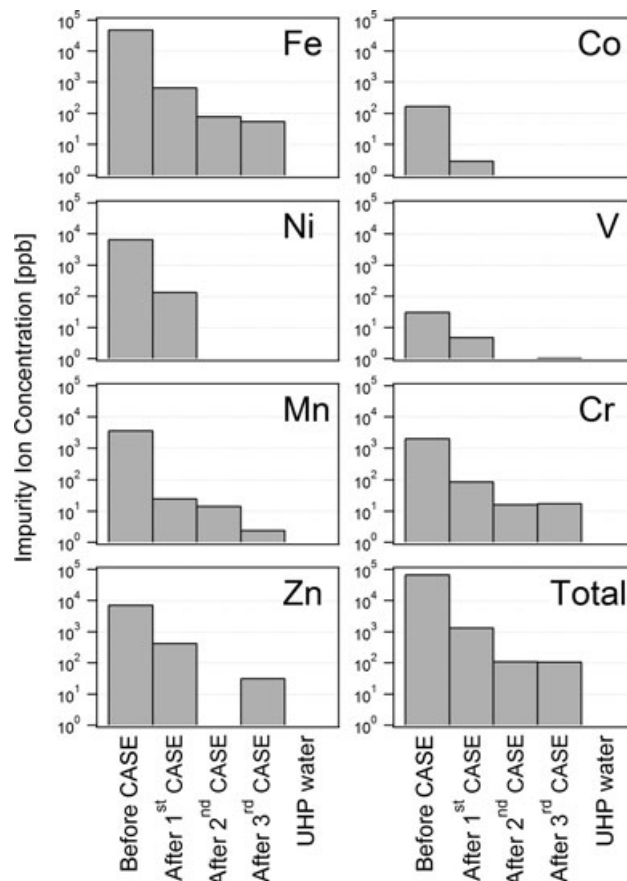
fication, even these precursors would result in a ZBLANI:  $\text{Yb}^{3+}$  with several tens of ppm of transition-metal contamination, still exceeding the impurity target range by 100–1000 fold. Clearly, additional purification is required for a sensitive application such as solid-state laser cooling.

Our strategy for preparing ultra-pure metal fluorides consists of (1) removing transition-metal impurities from an aqueous phase by CASE, (2) precipitation of the metal fluoride with hydrofluoric acid, (3) removing residual oxygen-based impurities (such as metal oxides, oxyfluorides,  $\text{OH}^-$ , and water) by drying and fluorination in hot hydrogen fluoride (HF) gas, followed by (4) synthesizing the glass in a water and oxygen-free clean environment. The aqueous phase in the CASE process is favorable because it enables the use of high quality starting materials such as metal oxides, carbonates, chlorides, and metals that can be dissolved in acid or water. But aqueous processing implies the challenge of subsequently removing residual water and oxides from precipitated “wet” binary metal fluorides. Therefore, the second step of drying and fluorination in hot HF gas is essential as it enables the preceding aqueous CASE process. Together, CASE and drying/fluorination in HF gas constitute a general purification method that is applicable to the synthesis of a wide range of metal fluorides.

## (2) Effectiveness of Chelate-Assisted Solvent Extraction

The effectiveness of removing transition-metal impurities from the aqueous metal-ion solutions was studied quantitatively by ICP-MS. The set of transition metals Cu, Fe, Co, Ni, V, Cr, Mn, and Zn was chosen based on the expected detrimental effects of some of these impurities on the efficiency of  $\text{Yb}^{3+}$ -doped laser-cooling materials.<sup>15</sup> The ICP-MS study was carried out for zirconium because  $\text{ZrF}_4$  amounts to more than half of the final ZBLANI glass composition (see Table II). The UHP water, used extensively in the CASE process, was also analyzed for transition-metal impurities, both to verify its purity and to establish a point of reference for the ICP-MS measurements. None of the eight different transition-metal ions was detected in the UHP water within the detection limits (low ppt) of the ICP-MS. We also analyzed the doubly distilled acids, the buffer solution, and the hydrogen peroxide (used in ICP-MS sample preparation). Transition-metal concentrations in these reagents were found to be negligible, indicating that any significant transition-metal impurities detected in the zirconium sample solutions were introduced by the  $\text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O}$  starting material.

The results of the ICP-MS study are summarized in Table III and illustrated in Fig. 1, which shows the concentration of each of the eight transition-metal impurities (on a log-scale, in ppb) at various stages in the CASE purification of the zirconium solution. No copper was found in any of the samples, and it is omitted from Fig. 1. The “Before CASE” sample represents the filtered and buffered aqueous  $\text{ZrCl}_2\text{O}$  solution taken directly before the first CASE step. This initial  $\text{ZrCl}_2\text{O}$  solution was found to be substantially contaminated, having a total of ~72500 ppb of the eight different transition metals probed by the ICP-MS, of which 71% was Fe. The remaining three samples shown in Fig. 1 were taken from the aqueous phase after each of the three



**Fig. 1.** Effectiveness of chelate-assisted solvent extraction (CASE) in purifying a  $\text{ZrCl}_2\text{O}$  solution as measured by ICP-MS (see Table III). The solution was analyzed before CASE, and after each of the three successive CASE steps (see Section II). No Cu was detected in any of the solutions within the detection limit of the ICP-MS (low ppt).

successive solvent extraction steps. The concentration of most of the eight transition metals decreased for each solvent extraction step. The first CASE step reduced the total concentration of the eight transition metals from ~72500 to ~1400 ppb, with the residual impurities consisting primarily of not only Fe, but also Zn and Cr. The second CASE step further reduced the total impurity concentration from ~1400 to ~100 ppb. The third CASE step did not reduce impurity levels any further and appeared to be ineffective. The extraction coefficients (percentage of impurity removed per extraction step) for the first CASE step were found to be 99.3% (Mn), 98.7% (Fe), 98.3% (Co), 98.0% (Ni), 95.6% (Cr), 94.1% (Zn), and 84.5% (V). These values are consistent with earlier reports of solvent extraction using the APDC chelate in a water/MIBK two-phase system.<sup>31,32,34</sup> These extraction coefficients also illustrate that at least two extraction steps are needed to reduce the initial concentration by 1000-fold. The extraction coefficients were generally lower for the second and third extraction steps (where applicable), which may be due to recontamination of the solution partially offsetting

the effect of the chelate at impurity concentrations <50 ppb. This is seen for Zn, Cr, and V (Table III), for which a slight increase in the concentration after the third extraction step was observed.

High-purity hydrofluoric acid was added to the aqueous solution after the third CASE step to precipitate  $(\text{NH}_4)_3\text{ZrF}_6$  which was then thermally decomposed to  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  [see Section II(2)]. The residual transition-metal impurities in the final zirconium solution (see Fig. 1) are therefore assumed to be representative of the purity in the final fluoride  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  before HF gas drying/fluorination. The measured impurity level of ~100 ppb compares favorably with the range of 10–100 ppb required for efficient optical refrigerator materials.<sup>15</sup>

### (3) Drying and Fluorination in HF Gas

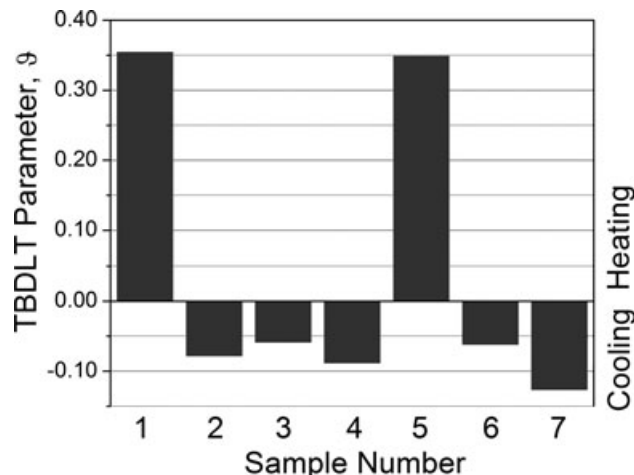
Purification of an aqueous phase by CASE is effective in reducing transition metals; however, it yields metal fluorides with residual oxygen-based impurities which can be equally detrimental in many applications, including solid-state optical refrigeration. Oxygen-based impurities can increase multi-phonon relaxation, increase the tendency of glass to crystallize, increase light scattering, and decrease chemical durability.<sup>41</sup> Treatment of metal fluorides in hot HF gas can remove oxygen impurities by two mechanisms: (1) surface water and water of crystallization evaporate from the fluorides or from oxyfluorides and oxides as they are heated and (2) remaining oxides, hydroxides, and oxyfluorides, which are thermodynamically less stable than the respective fluoride, react with HF to form the metal fluoride by releasing water into the gas phase.

Samples 1–3 (see Table II) were made from fluorides which were processed in HF gas at 550°C.<sup>37,38</sup> We found that metal fluorides exposed to HF at this temperature consistently had a grayish tint, and a brownish gelatinous residue emerged from the output port of the drying vessel during the HF process. These residues were likely a result of corrosion of the Inconel Alloy 600 parts and the glassy-carbon liner of the apparatus. We have found that lowering the drying temperature to 300°C eliminated these corrosion residues and resulted in white metal fluoride powder. This lower HF process temperature is also suggested by the results of Kwon *et al.*, which have shown that finely powdered  $\text{CeO}_2$ ,  $\text{Nd}_2\text{O}_3$ , and  $\text{SrO}$  can be quantitatively converted to the respective fluorides by exposure to 33 vol% HF in argon at 300°C in less than 1 h.<sup>42</sup> We, therefore expect the drying/fluorination in the apparatus described herein [19 h at 300°C in ~7 vol% HF in argon; see Section II(3)] to be highly effective in removing oxygen-based impurities.

### (4) Effect on Solid-State Laser-Cooling Performance

The laser-cooling performance can be measured by two-band differential luminescence thermometry (TBDLT), a non-contact technique that monitors the luminescence from a sample and deduces laser-induced internal temperature changes from changes in the intensity distribution of the luminescence spectrum as the pump laser is cycled on and off.<sup>39,40</sup> In practice, the  $\text{Yb}^{3+}$  luminescence is split into two spectral bands. As the pump laser is turned on, the relative band intensity changes due to a change in the local temperature (laser-induced cooling or heating), and it approaches a new equilibrium value according to a power law with exponent  $\theta$ .<sup>40</sup> This TBDLT parameter  $\theta$  is a measure of the laser-induced internal temperature change, where  $\theta > 0$  and  $\theta < 0$  indicate internal heating and cooling, respectively. Therefore,  $\theta$  can be used as an indirect measure of the aggregate impurity concentration.

Figure 2 is a quantitative demonstration of the enhancement of laser-cooling performance by applying the purification methods described in this study. Sample 1 clearly illustrates that even the best commercial metal fluorides have



**Fig. 2.** Solid-state laser-cooling performance of the samples prepared in this study (Table III). The TBDLT parameter,  $\theta$ , (measured at 300 K) is proportional to the laser-induced change in internal sample temperature: a positive and negative  $\theta$  corresponds to laser-induced heating and cooling, respectively. Samples 2–4 exhibited laser cooling, indicating that the CASE purification in combination with drying and fluorination in hot HF gas were successful in significantly reducing transition-metal and oxygen-based impurities.

insufficient purity to enable laser cooling; this sample showed substantial laser-induced heating ( $\theta > 0$ ) even at room temperature. The use of CASE purification combined with drying and fluorination in hot HF gas provided a substantial improvement of the laser-cooling performance. Samples 2, 3, and 4 represent various stages of the development of the CASE/HF process, and they all achieved laser-induced cooling ( $\theta < 0$ ). Note that sample 4, which was prepared from metal fluorides that were treated in HF gas at 300°C instead of 550°C [see Section III(3)], had the best laser-cooling performance of all samples prepared in this study. The  $\text{Yb}^{3+}$  concentration was increased from 1 to 2 mol% in sample 5, which resulted in substantial laser-induced heating. The rate of energy migration among  $\text{Yb}^{3+}$  ions increases with increasing  $\text{Yb}^{3+}$  concentration, and some of the excitations can find impurity sites where non-radiative relaxation takes place. This process is more efficient in the 2%  $\text{Yb}^{3+}$ -doped sample 5 compared to the 1%  $\text{Yb}^{3+}$ -doped sample 4. The fact that sample 5 showed substantial heating is direct evidence that some transition-metal and/or oxygen-based impurities are still present in the material. Also note that the use of  $\text{ZrF}_4$  purified by sublimation (provided by the University of Bern; sample 6) resulted in a glass that cooled, albeit not as much as the best sample fabricated from precursors purified by the CASE process. This shows that the CASE/HF process is more effective in removing impurities from  $\text{ZrF}_4$  compared to sublimation. Sample 7 is a commercial ZBLAN:Yb<sup>3+</sup> fluoride glass that was obtained from IPG Photonics. It was selected as the exceptional top performer from several dozen nominally identical commercial ZBLAN:Yb<sup>3+</sup> batches that varied widely in their laser-cooling performance (both heating and cooling were observed) and, by inference, aggregate impurity concentration. This substantial batch-to-batch performance variation in commercial ZBLAN:Yb<sup>3+</sup> samples illustrates the sensitivity of the laser-cooling efficiency to impurities. Sample 4 showed the best laser-cooling performance of the samples produced by the CASE/HF process in this study. Whereas it did not outperform the best commercial sample 6, we note that the CASE/HF process yielded consistent batch-to-batch performance. Therefore, further optimization of the baseline process presented herein is expected to result in materials of both superior and consistent performance.

#### IV. Conclusions

A comprehensive purification method suited for all of the ZBLAN:Yb<sup>3+</sup> glass constituents was demonstrated for the first time. We showed that CASE using APDC as a chelate and MIBK/water as a two-phase system is effective in removing problematic transition-metal impurities from a ZrCl<sub>2</sub>O solution. The transition-metal contamination was reduced by almost 1000-fold, and a residual transition-metal concentration of ~100 ppb was achieved. Subsequent drying and fluorination of the resulting metal fluorides in hot hydrogen fluoride gas proved effective in removing residual oxygen-based impurities, as confirmed by laser-cooling measurements. This work is focused on optimization of CASE with the APDC chelate, finding other chelates/solvent systems with improved characteristics, and further developing the process of drying and fluorination in HF gas. The suite of processes presented herein is applicable to the preparation of a wide range of ultra-pure binary fluorides, and it establishes a foundation for the growth of a variety of fluoride crystals and glasses for demanding photonic applications.

#### Acknowledgments

We thank Dr. Karl Krämer at the Department of Chemistry and Biochemistry, University of Bern, Switzerland, for his assistance with the design of the hydrogen fluoride gas drying apparatus and for providing the sublimated ZrF<sub>4</sub> used for the synthesis of Sample 6. We gratefully acknowledge the support of the Air Force Office of Scientific Research under the Multidisciplinary University Research Initiative (MURI) program.

#### References

- T. M. Bloomstein, M. W. Horn, M. Rothschild, R. R. Kunz, S. T. Palmacci, and R. B. Goodman, "Lithography with 157 nm Lasers," *J. Vac. Sci. Technol. B*, **15**, 2112–6 (1997).
- S. Sudo, "Progress in Optical Fiber Amplifiers"; pp. 19–21 in *Current Trends in Optical Amplifiers and their Applications*, Edited by T. P. Lee. World Scientific, NJ, 1996.
- T. G. Brown, "Optical Fibers and Fiber-Optic Communications"; pp. 1–49 in *Fiber Optics Handbook: Fiber, Devices and Systems for Optical Communications*, Edited by M. Bass and E. W. van Stryland. McGraw-Hill, New York, 2002.
- S. Bedo, M. Pollnau, W. Luthy, and H. P. Weber, "Saturation of the 2.71  $\mu$ m Laser Output in Erbium-Doped ZBLAN Fibers," *Opt. Commun.*, **116**, 81–6 (1995).
- X. Zhu and R. Jain, "Numerical Analysis and Experimental Results of High-Power Er/Pr:ZBLAN 2.7  $\mu$ m Fiber Lasers with Different Pumping Designs," *Appl. Optics*, **45**, 7118–25 (2006).
- T. Sakamoto, M. Shimizu, T. Kanamori, Y. Terunuma, Y. Ohishi, M. Yamada, and S. Sudo, "1.4- $\mu$ m-Band Gain Characteristics of a Tm-Ho-Doped ZBLAN Fiber Amplifier Pumped in the 0.8- $\mu$ m Band," *IEEE Photonics Technol. Lett.*, **7**, 983–5 (1995).
- B. Pedersen, W. J. Miniscalco, and R. S. Quimby, "Optimization of Pr<sup>3+</sup>-ZBLAN Fiber Amplifiers," *IEEE Photonics Technol. Lett.*, **4**, 446–8 (1992).
- D. F. Anderson, "Cerium Fluoride – A Scintillator for High-Rate Applications," *Nucl. Instrum. Meth. Phys. Res. A*, **287**, 606–12 (1990).
- E. Auffray, D. Bouttet, I. Dafinei, J. Fay, P. Lecoq, J. A. Mares, M. Martini, G. Maze, F. Meinardi, and B. Moine, "Cerium Doped Heavy Metal Fluoride Glasses, a Possible Alternative for Electromagnetic Calorimetry," *Instrum. Meth. Phys. Res. A*, **380**, 524–36 (1996).
- J. Freek Suijver, "Upconversion Phosphors"; pp. 133–75 in *Luminescence: From Theory to Applications*, Edited by C. Ronda. Wiley-VCH, Weinheim, 2008.
- R. I. Epstein and M. Sheik-Bahae, "Optical Refrigeration in Solids: Fundamentals and Overview"; pp. 1–32 in *Optical Refrigeration. Science and Applications of Laser Cooling of Solids*, Edited by R. I. Epstein and M. Sheik-Bahae. Wiley, Weinheim, 2009.
- W. G. Rellergert, D. DeMille, R. R. Greco, M. P. Hehlen, J. R. Torgerson, and E. R. Hudson, "Constraining the Evolution of the Fundamental Constants with a Solid-State Optical Frequency Reference Based on the Th-229 Nucleus," *Phys. Rev. Lett.*, **104**, 200802 (2010).
- Y. Ohishi, S. Mitachi, T. Kanamori, and T. Manabe, "Optical Absorption of 3d Transition-Metal and Rare-Earth Elements in Zirconium Fluoride Glasses," *Phys. Chem. Glasses*, **24**, 135–40 (1983).
- S. Mitachi, T. Miyashita, and T. Manabe, "Preparation of Fluoride Optical Fibres for Transmission in the Mid-Infrared," *Phys. Chem. Glasses*, **23**, 196–201 (1982).
- M. P. Hehlen, R. I. Epstein, and H. Inoue, "Model of Laser Cooling in the Yb<sup>3+</sup>-Doped Fluorozirconate Glass ZBLAN," *Phys. Rev. B*, **75**, 144302 (2007).
- E. O. Gbogi, K.-H. Chung, and C. T. Moynihan, "Surface and Bulk OH<sup>-</sup> Infrared Absorption in ZrF<sub>4</sub>- and HfF<sub>4</sub>-Based Glasses," *J. Am. Ceram. Soc.*, **64**, C-51–3 (1981).
- P. W. France, S. F. Carter, J. R. Williams, and K. J. Beales, "OH-Absorption in Fluoride Glass Infrared Fibres," *Electron. Lett.*, **20**, 607–8 (1984).
- L. J. B. Vacha, C. T. Moynihan, B. B. Harbison, K. Cadien, R. Mossadegh, and P. C. Schultz, "Hermetic Coatings for Bulk Fluoride Glasses and Fibres," *Int. J. Opt. Sensors*, **2**, 297–304 (1987).
- H. Poignant, pp. 35–56 in *Halide Glasses for Infrared Fiber Optics*, Edited by R. M. Almeida. Nijhoff, Amsterdam, 1987.
- P. Kaiser, A. R. Tynes, H. W. Astle, A. D. Pearson, W. G. French, R. E. Jaeger, and A. H. Cherin, "Spectral Losses of Unclad Vitreous Silica and Soda-Lime-Silicate Fibers," *J. Opt. Soc. Am.*, **63**, 1141–8 (1973).
- P. W. France, S. F. Carter, and J. R. Williams, "NH<sub>4</sub><sup>+</sup> Absorption in Fluoride Glass Infrared Fibres," *J. Am. Ceram. Soc.*, **67**, C243–4 (1984).
- M. Poulain and M. Saad, "Absorption Loss Due to Complex Anions in Fluorozirconate Glasses," *J. Lightwave Tech.*, **2**, 599–602 (1984).
- J. M. Jewell, J. Coon, and J. E. Shelby, "The Extinction Coefficient for CO<sub>2</sub> Dissolved in a Heavy-Metal Fluoride Glass," *Mat. Sci. Forum.*, **32–33**, 421–6 (1988).
- D. R. MacFarlane, P. J. Newman, A. Voelkel, and E. Snitzer, "Methods of Purification of Zirconium Tetrafluoride for Fluorozirconate Glass," *J. Am. Ceram. Soc.*, **85**, 1610–2 (2002).
- B. E. Kinsman and R. Hanney, "Preparation and Purification of Metal Fluorides for Crystals and Glasses," *Adv. Materials for Opt. and Elect.*, **5**, 109–15 (1995).
- A. M. Mailhot, A. Elyamani, and R. E. Riman, "Reactive Atmosphere Synthesis of Sol-Gel Heavy Metal Fluoride Glasses," *J. Mater. Res.*, **7**, 1534–40 (1992).
- C. T. Moynihan, M. G. Drexhage, B. Bendow, M. Saleh Boulos, K. P. Quinlan, K. H. Chung, and E. Gbogi, "Composition Dependence of Infrared Edge Absorption in ZrF<sub>4</sub> and HfF<sub>4</sub> Based Glasses," *Mater. Res. Bull.*, **16**, 25–30 (1981).
- M. Jardin, J. Guery, and C. Jacoboni, "Preparation in Vapour State of Fluoride Glass Components by a Chemical Vapour Deposition Process," *J. Non-Cryst. Solids*, **184**, 204–8 (1995).
- Y. Nishida, K. Fujiura, H. Sato, S. Sugawara, K. Kobayashi, and S. Takahashi, "Preparation of ZBLAN Fluoride Glass Particles by Chemical Vapor Deposition Process," *Jpn. J. Appl. Phys. Part 2*, **31**, L1692–4 (1992).
- K. Fujiura, Y. Ohishi, M. Fujiki, T. Kanamori, and S. Takahashi, "Process for the Preparation of Fluoride Glass and Process for the Preparation of Optical Fiber Preform Using the Fluoride Glass," *U.S. Patent*, **5** [071] 460 (1991).
- H. Malissa and E. Schöffmann, "Über die Verwendung von substituierten Dithiocarbamaten in der Mikroanalyse," *Mikrochim. Acta*, **1**, 187–202 (1955).
- M. Arnac and G. Verboom, "Solubility Product Constants of Some Divalent Metal Ions with Ammonium Pyrrolidine Dithiocarbamate," *Anal. Chem.*, **46**, 2059–61 (1974).
- D. Bertrand, J. Guery, and C. Jacoboni, "Fe,Co,Ni,Cu Trace Metal Analysis in ZBLAN Fluoride Glasses," *J. Non-Cryst. Solids*, **161**, 32–5 (1993).
- R. R. Brooks, M. Hoashi, S. M. Wilson, and R. Q. Zhang, "Extraction into Methyl Isobutyl Ketone of Metal Complexes with Ammonium Pyrrolidine Dithio-Carbamate Formed in Strongly Acidic Media," *Anal. Chim. Acta*, **217**, 165–70 (1989).
- J. D. Kinrade and J. C. van Loon, "Solvent Extraction for Use with Flame Atomic Absorption Spectrometry," *Anal. Chem.*, **46**, 1894–8 (1974).
- Z. Ling, Z. Chengshan, D. Gaoxian, and W. Kangang, "ZrOCl<sub>2</sub> for Fluoride Glass Preparation," *J. Non-Cryst. Solids*, **140**, 331–4 (1992).
- R. Burkharter, I. Dohnke, and J. Hulliger, "Growing of Bulk Crystals and Structuring Waveguides of Fluoride Materials for Laser Applications," *Prog. Cryst. Growth Charact. Mater.*, **42**, 1–64 (2001).
- K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen, and S. R. Lüthi, "Hexagonal Sodium Yttrium Fluoride Based Green and Blue Emitting Upconversion Phosphors," *Chem. Mater.*, **16**, 1244–51 (2004).
- W. M. Patterson, D. V. Seletskiy, M. Sheik-Bahae, R. I. Epstein, and M. P. Hehlen, "Measurement of Solid-State Optical Refrigeration by Two-Band Differential Luminescence Thermometry," *J. Opt. Soc. Am. B*, **27**, 611–8 (2010).
- W. M. Patterson, M. Sheik-Bahae, R. I. Epstein, and M. P. Hehlen, "Model of Laser-Induced Temperature Changes in Solid-State Optical Refrigerators," *J. Appl. Phys.*, **107**, 063108 (2010).
- M. Poulain, J. Lucas, and P. Brun, "Fluorated Glass from Zirconium Tetrafluoride – Optical Properties of a Doped Glass in Nd<sup>3+</sup>," *Mat. Res. Bull.*, **10**, 243–6 (1975).
- S. W. Kwon, E. H. Kim, B. G. Ahn, J. H. Yoo, and H. G. Ahn, "Fluorination of Metals and Metal Oxides by Gas-Solid Reaction," *J. Ind. Eng. Chem.*, **8**, 477–82 (2002).